

Solid Oxide Fuel Cells (SOFCs) for the Direct Oxidation of Methane

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Introduction

This newly funded project is merging the optimization of yttria-stabilized zirconia (YSZ)-based mixed-conducting electrodes with the development of anodes for the direct oxidation of methane. A mixed-conducting YSZ-based electrode has a number of advantages; these include enhanced mechanical and chemical compatibility with the YSZ electrolyte, an increased charge-transfer reaction area resulting in a lower electrode overpotential, and greater tolerances to gas impurities (e. g. sulfur in fuel gases)

Direct oxidation of methane in SOFCs avoids the equilibrium limitations of the steam-reforming reaction for low-temperature operation and the necessity of having a separate steam-reforming reactor. Our ultimate goal in merging developments from these two areas of research is to develop reduced-temperature SOFCs which are robust, inexpensive to fabricate, and can be operated at 600 to 800°C.

Problems

The work involving mixed-conducting YSZ-based electrodes is at a more advanced stage than the direct-oxidation work. We have demonstrated that the overpotential losses of YSZ-based electrodes can be lower than the electrodes currently used in SOFCs, and that a YSZ-electrolyte cell with YSZ-doped electrodes can exhibit attractive current and power densities. We are now determining the best dopants for optimum cell power densities at reduced temperatures, and are minimizing interfacial resistances and overpotential losses in thin-film YSZ cells having YSZ-based electrodes containing the optimum dopants. We are also collaborating to develop an attractive anode for the direct oxidation of methane.

A key limitation for the direct oxidation of methane, particularly at temperatures below 800°C, is the relatively low reactivity of methane. This is the reason essentially all SOFC designs require that methane first be converted to hydrogen through steam reforming. The question is why can't one carry out the oxidation of methane directly? The rates required in a fuel cell are not extremely high. For a current density of 1 Amp/cm², a porous anode with only 1 cm² of catalytic surface area per cm² of planar fuel cell (very low for a porous catalyst) would require a turnover frequency of less than 10, a reasonable value for oxidation catalysts.

To answer the question posed above, one needs to consider what is actually occurring at the anode in conventional SOFCs and consider the likely reasons why most attempts at direct oxidation of methane have failed. First, while the Ni-zirconia cermet commonly used at the anode is sometimes referred to as an “electrocatalyst”, there is no evidence that it performs this function. The Ni really acts only as a steam reforming catalyst and current carrier. The H_2 formed by steam reforming is so reactive that it can probably be oxidized on the YSZ surface at the typical temperatures used in SOFCs. There is considerable evidence from the literature that oxygen anions from the YSZ electrolyte never migrate to the anode surface when metal catalysts are used. Oxygen anions can diffuse from YSZ to mixed-conducting oxides, such as ceria and bismuth (1); and some success has been achieved for the direct oxidation of methane using these materials. However, no known oxide has achieved acceptable rates.

Previous Results

Mixed-Conducting YSZ-Based Electrodes

In the cathodic environment (air) of a SOFC, the best dopant to produce a YSZ-based electrode is one which provides the highest p-type electronic conductivity with no significant degradation of the oxygen-ion conductivity. We have successfully synthesized mixed-conducting YSZ-based cathodes by dissolving terbia ($TbO_{1.75}$) into YSZ. The Y8ZTb20 (YSZ containing 8 mole % yttria and 20 mole % terbia) and Y8ZTb30 solid solutions have excellent mixed (oxygen-ion and p-type electronic)-conductivities (2, 3). Fig. 1 shows that the overpotentials of six mixed-conducting Y8ZTb30 and Y8ZTb20 cathodes (having different preparation methods and thicknesses) are smaller than those of the similarly prepared platinum and the currently used $La_{0.85}Sr_{0.15}MnO_3$ (LSM) cathodes (4, 5). This is believed due to the increased charge-transfer-reaction area for the mixed-conducting Y8ZTb cathodes.

We have also dissolved titania in Y8SZ and Y12SZ to obtain a YSZ-based anode. (6,7). The n-type electronic conductivity of YZTi becomes significant when the oxygen pressure is below $\sim 10^{-15}$ atm due to the presence of both Ti^{+3} and Ti^{+4} cations and the associated electron hopping between them in these very low oxygen-pressure environments (7, 8). The n-type electronic conductivity of titanium-doped YSZ increases with decreasing oxygen pressure and with increasing titania concentration and temperature (7, 8). Because typical oxygen pressures at the fuel-gas anode in a SOFC vary from 10^{-15} to 10^{-22} atm, a YSZ-based anode containing titanium cations should have excellent mixed (oxygen-ion and n-type electronic) conductivity. Fig. 2 shows that the Y8/ZTi20 and Y12ZTi20 anodes have much lower overpotentials than those of a Ni/YSZ cermet anode (4, 7).

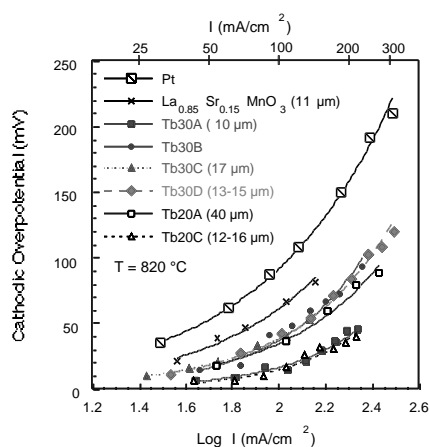


Fig. 1 Comparison of the overpotentials of the Y8ZTb20 and Y8ZTb30 cathodes with Pt and $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$ cathodes in air.

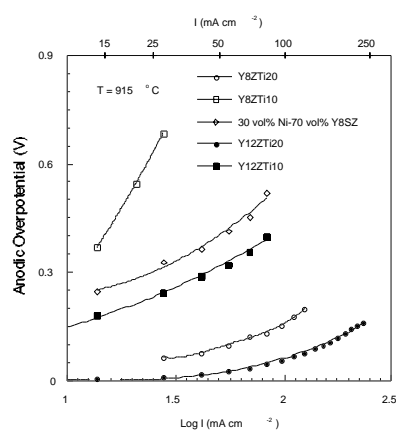


Fig. 2 Comparison of the overpotentials of the Y8ZTi20, Y8ZTi10, Y12ZTi10, and Y12ZTi20 anodes with that of a Ni(30 vol%)/Y8SZ cermet anode at 2×10^{-18} atm PO_2

The cell voltage variation with current density for two Y8ZTb/Y8SZ/Y8ZTi or Y12ZTi cells (4, 7) are shown in Figs. 3 and 4. The improved cell performance shown in Fig. 4 over that shown in Fig. 3 is consistent with the Y12ZTi20 anode overpotentials being lower than those of the Y8ZTi20 anode (as shown in Fig. 2). This research has resulted in two patents (9, 10).

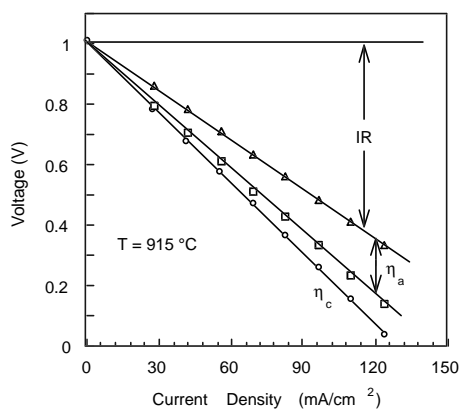


Fig. 3 Single oxide cell performance at 915 °C for the cell: Air, Y8ZTb20 / Y8SZ / Y8ZTi20, $\text{PO}_2 = 2 \times 10^{-18}$ atm.

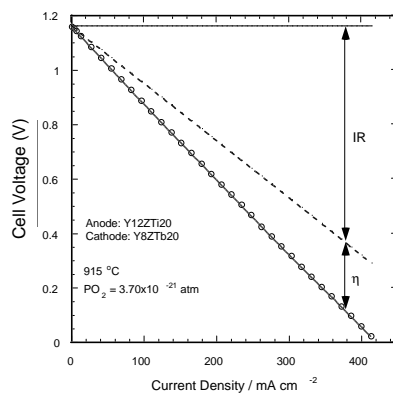


Fig. 4 Cell performance of the single oxide cell: Air, Y8ZTb20 / Y8SZ / Y12ZTi20

The power densities of these cells are not yet comparable to the largest ones reported for thin film (~ 5 -10 mm) YSZ cells, principally because the thickness of our YSZ electrolyte was much larger (~ 1,500 mm). However, our results for single-cells with mixed-conducting YSZ-based electrodes demonstrate that these electrodes can be attractive competitors in the next generation SOFCs. For example, we estimate that the power density of our mixed-conducting YSZ-based electrode cell at 800°C with a thin-film YSZ-electrolyte thickness of 10 mm can be as high as ~ 2.6 W/cm², depending on the thickness and morphology of the electrodes. In obtaining this maximum number, we have assumed that the major cell losses are ohmic ones, which is justified by the lower electrode overpotential (η) losses illustrated in Figs. 1 and 2. Furthermore, our YSZ-based electrode overpotentials at higher current densities can be reduced by optimizing dopant compositions and morphology. We are also working collaboratively in the develop of new anodes for the direct oxidation of methane.

Anodes for the Direct Oxidation of Methane

Automotive, emissions-control catalysts have the properties one is looking for in a SOFC anode. Automotive catalysts contain as much as 40 wt % ceria, with a very small amount of precious metals like Pt, Pd and Rh. The ceria plays the role of oxygen-storage component, a critical component for maintaining the oxygen stoichiometry in the exhaust. To achieve the oxygen-exchange rates needed in automotive applications, ceria must be in intimate contact with the precious metal and it seems clear that oxygen transport between the ceria and the precious metal plays a fundamental part in oxygen storage. For example, in our own work in this area, we have shown that small Rh particles supported on ceria films appear to be oxidized by the ceria in vacuum at temperatures close to room temperature (11). These ideas have obvious application to anode design in SOFCs. High catalytic activity for oxidation of methane in a SOFC anode is not useful if one cannot provide oxygen to the catalyst surface, but the materials used in automotive catalysis provide both high catalytic activities and high oxygen transfer capabilities.

We have used anodes consisting of samaria-doped ceria (SDC), of varying thickness (ie. varying catalytic surface area), with and without Rh added as a dopant (12). The current carrier in our test cells was a Au mesh attached directly to the YSZ electrolyte. Two key features of this cell are noteworthy. First, the catalytic and current carrying functions in our test cell were separate. Au was used to carry current in our studies simply because of its inert catalytic properties. Second, by placing the current carrier next to the electrolyte, electronic and ionic resistances in the anode due to changing the thickness of the catalyst should not strongly affect the performance.

The results obtained using hydrogen as a fuel were largely independent of either anode thickness or presence of the metal at 800°C. The current-voltage characteristics were essentially identical on all four cells tested, even when the thickness of the SDC was increased by a factor of 10, whether or not Rh was added as a dopant. Because the electrolyte in our cells was relatively thick (1.7 mm) it appears that the performance was completely limited by oxygen-ion conductivity in the YSZ. The same was not true when dry methane was used as a fuel. First, increasing the thickness (surface area) of the SDC by a factor of 10 had the effect of increasing the open-circuit voltage from ~0.2 volts to 0.9 volts, as well as increasing the maximum current density from 2 mA/cm² to ~10

mA/cm². Both performance measures were less than that obtained using hydrogen as a fuel, where the maximum current density was greater than 30 mA/cm². More interesting, when Rh was added to the anodes by impregnation of Rh(NO₃)₃, the performance of the cells changed dramatically. Independent of the SDC thickness, the maximum current density and power generation increased to the level found using hydrogen as a fuel.

The above results demonstrate several points but also raise several questions. For the SDC anodes without Rh, it appears that catalytic activities of the anode limited the performance of the cell. With the addition of Rh as a dopant, however, it appears that the performance was no longer limited by the anode. Clearly, further work is needed to determine the point at which anode catalytic properties will limit performance. The results do, however, prove that direct oxidation of methane is feasible with optimized anodes.

Future Work

Future work will be focussed towards optimising mixed-conducting YSZ-based electrodes and developing anodes for the direct oxidation of methane. Concepts from both areas will be incorporated in developing SOFCs for the direct oxidation of methane.

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